

Comment on: Failure of the work-Hamiltonian connection for free energy calculations

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We argue that the apparent failure of the work-Hamiltonian connection for free energy calculations reported by Vilar and Rubí (cond-mat arXiv:0704.0761v2) stems from their incorrect expression for the work.

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In a recent preprint, Vilar and Rubí [1] have argued that the pivotal connection between the microscopic work W performed by a time-dependent force and the energy change associated with its change in state cannot be used to estimate free-energy changes. Since in several occasions some groups have exploited the measure of work applied on microscopic systems to evaluate its free energy landscape, the failure of this connection would have far-reaching consequences.

In the present note we reevaluate Vilar and Rubí’s arguments to test their validity. We find that they rest on an incorrect expression of the work to be evaluated, and that therefore, if one measures the correct quantity, which is experimentally accessible, it is possible to exploit the work-free energy relation in order to gather thermodynamical information on microscopic systems.

Let us consider a system whose microscopic state is described by the coordinate x , and governed by the hamiltonian $H(x, \mu)$ which depend on an external parameter μ which can be manipulated. The equilibrium state for a given value of μ is described by the canonical distribution

$$p_{\mu}^{\text{eq}}(x) = \frac{e^{-H(x, \mu)/T}}{Z_{\mu}}, \quad (1)$$

where the partition function Z_{μ} is given by

$$Z_{\mu} = \int dx e^{-H(x, \mu)/T}. \quad (2)$$

The free energy G_{μ} associated with the given value of μ is given by

$$G_{\mu} = -T \log Z_{\mu}. \quad (3)$$

Let us now evaluate the change in G_{μ} as μ varies from, say, $\mu = 0$ to a final value μ . One has

$$\begin{aligned} \frac{\partial G_{\mu}}{\partial \mu} &= (-T) \frac{1}{Z_{\mu}} \int dx e^{-H(x, \mu)/T} \left(-\frac{1}{T} \frac{\partial H(x, \mu)}{\partial \mu} \right) \\ &= \left\langle \frac{\partial H}{\partial \mu} \right\rangle_{\mu}, \end{aligned} \quad (4)$$

where $\langle A \rangle_{\mu}$ denotes the average of the function $A(x)$ with respect to the canonical distribution (1). Thus

$$\Delta G = G_{\mu} - G_0 = \int_0^{\mu} d\mu' \left\langle \frac{\partial H}{\partial \mu} \right\rangle_{\mu'}. \quad (5)$$

We now define the *reversible work* W_{rev} as the quantity which appears on the rhs of this expression:

$$W_{\text{rev}} = \int_0^{\mu} dW_{\text{rev}} = \int_0^{\mu} d\mu' \left\langle \frac{\partial H}{\partial \mu} \right\rangle_{\mu'}. \quad (6)$$

This definition is an immediate consequence of equation (128.1), p. 535 of Tolman’s book [2]. Its contents is explained by Tolman [2, p. 527] in the following way:

The concept of *work* performed by a thermodynamic system on its surroundings depends on the possibility of changing the values of external parameters for the system, which have the nature of generalized coordinates. In the thermodynamic treatment, when a small variation is made in the value of such an external coordinate, the work done can be set equal to the product of that variation by the corresponding generalized force exerted by the system on its surroundings, and can be regarded as equal to the (potential) energy thereby transferred to external bodies. [...] In the corresponding statistical treatment we can assign to all the systems in the representative ensemble the same value of the external coordinates as those of the thermodynamic system of interest, and can represent the corresponding generalized forces by their average values in that ensemble. The work done and the energy thereby transferred to external bodies can then be represented by its average value for the ensemble, as given by the product of the definite value of the displacement with the average value of the corresponding generalized force.

With this definition, the equality between ΔG and W_{rev} is trivially satisfied:

$$\Delta G = W_{\text{rev}}. \quad (7)$$

It is important to remark that, *by definition*, the reversible work is a non-fluctuating quantity (the equilibrium average of an observable). Thus, if we evaluate, e.g., $\langle e^{-W_{\text{rev}}/T} \rangle$, we have

$$\langle e^{-W_{\text{rev}}/T} \rangle = e^{-W_{\text{rev}}/T} = \exp \left\{ \int_0^\mu d\mu' \left\langle \frac{\partial H}{\partial \mu} \right\rangle_{\mu'} \right\}. \quad (8)$$

On the other hand, because of (7), one has

$$\langle e^{-W_{\text{rev}}/T} \rangle = e^{-\Delta G/T}, \quad (9)$$

and, because of (3),

$$e^{-\Delta G/T} = e^{-(G_\mu - G_0)/T} = \frac{Z_\mu}{Z_0}. \quad (10)$$

Equation (9) represents the special case of Jarzynski's equality [3] which holds in the limit of reversible manipulation. Let us define the fluctuating infinitesimal work, $dW(x, \mu)$ as the quantity whose average is given by $dW_{\text{rev}}(\mu)$:

$$dW(x, \mu) = d\mu \frac{\partial H(x, \mu)}{\partial \mu}. \quad (11)$$

Then the Jarzynski equality states that

$$\langle e^{-W/T} \rangle = e^{-\Delta G/T}. \quad (12)$$

In this expression, W is the fluctuating total work

$$W = \int dW = \int_{t'=0}^{t'=t} dt' \dot{\mu}(t') \left. \frac{\partial H(x, \mu)}{\partial \mu} \right|_{x=x(t'), \mu=\mu(t')}, \quad (13)$$

and the average is taken over all realizations of the process $x(t)$ with a given manipulation protocol $\mu(t)$.

In order to give a more definite interpretation of this quantity, let us consider, as in [1], the simple case of a particle bound to the origin by a spring of Hooke's constant k and to which a time-dependent force $f(t)$ is applied. We then take f as a generalized coordinate, and write $H(x, f)$ as

$$H(x, f) = \frac{1}{2} k x^2 - f x. \quad (14)$$

Then

$$\frac{\partial H}{\partial f} = -x, \quad (15)$$

and

$$dW = -x df. \quad (16)$$

On the other hand, the *mechanical* work that the external force exerts on the system is given by

$$dW_{\text{mech}} = f dx. \quad (17)$$

Note that

$$dW - dW_{\text{mech}} = -d(fx). \quad (18)$$

We see that the work appearing in Jarzynski's equality is not equal to the mechanical work exerted on the system. The difference between the two works is equal to the variation of the potential energy associated with the force. It is therefore no surprise that, if one evaluates the integral of the mechanical rather than the thermodynamical work, one obtains an incorrect estimate of the free-energy difference.

We can now straightforwardly check the validity of the relation between the reversible work and the free energy, provided the full Hamiltonian is taken into account. We have, of course,

$$dW_{\text{rev}} = -df \langle x \rangle_f, \quad (19)$$

where $\langle x \rangle_f$ is the equilibrium position of the particle at force f :

$$\langle x \rangle_f = \frac{f}{k}. \quad (20)$$

Thus

$$\Delta G = - \int df \langle x \rangle_f = - \frac{f^2}{2k} = - \frac{1}{2} k \langle x \rangle_f^2. \quad (21)$$

This quantity is equal to the one obtained from the partition function, as can be trivially checked. It is negative, because the positive variation of the spring potential energy is more than compensated by the drop in the potential energy of the applied force. One can imagine, e.g., that the guide to which is constrained the particle is made rotated by an angle θ around the origin in a vertical plane. Then $f = mg \sin \theta$, and, at equilibrium, the height of the particle has dropped to $z = -\langle x \rangle_f \sin \theta$, with a corresponding gravitational potential energy drop equal to mgz .

Of course nothing prevents us to take explicitly into account this contribution, in order to evaluate the change of $E - TS$, where E is the *internal* energy. It is sufficient to subtract the potential of the applied force. This is indeed what is routinely made when estimating the free energy landscapes from manipulation experiments, following the suggestions of Hummer and Szabo [4] and several others.

Let us now consider the second example discussed by Vilar and Rubí [1], namely a harmonically bound particle subject to a harmonic time-dependent force:

$$H(x, X) = \frac{1}{2} k x^2 + \frac{1}{2} K (x - X)^2. \quad (22)$$

By expanding this expression, we obtain

$$H(x, X) = \frac{1}{2}(k + K)x^2 - KXx + \frac{1}{2}KX^2. \quad (23)$$

Then

$$dW = -dX K(x - X). \quad (24)$$

Of course

$$dW_{\text{rev}} = -dX K(\langle x \rangle_X - X), \quad (25)$$

where $\langle x \rangle_X$ is the average displacement of the particle when the center of the harmonic trap is placed at X :

$$\langle x \rangle_X = \frac{K}{k + K}X. \quad (26)$$

Thus

$$\begin{aligned} \Delta G &= \int dW_{\text{rev}} = \int_0^X dX' K \left(1 - \frac{K}{k + K}\right) X' \\ &= \frac{1}{2} \frac{kK}{k + K} X^2 = \frac{1}{2} \frac{k(k + K)}{K} \langle x \rangle_X^2. \end{aligned} \quad (27)$$

This result is different from that reported by Vilar and Rubí, since it takes into account also the change in the potential energy U of the applied force.

Let us evaluate the change of $\langle U \rangle$. We have

$$\langle U \rangle_0 = \frac{1}{2}K \langle x^2 \rangle_0 = \frac{1}{2}K \langle \Delta x^2 \rangle_0; \quad (28)$$

$$\begin{aligned} \langle U \rangle_X &= \frac{1}{2}K \left\langle (x - X)^2 \right\rangle_X \\ &= \frac{1}{2}K \left[(\langle x \rangle_X - X)^2 + \langle \Delta x^2 \rangle_X \right]. \end{aligned} \quad (29)$$

In our case, $\langle \Delta x^2 \rangle_0 = \langle \Delta x^2 \rangle_X$. Thus

$$\begin{aligned} \langle U \rangle_X - \langle U \rangle_0 &= \frac{1}{2}K (\langle x \rangle_X - X)^2 \\ &= \frac{1}{2}K \left(1 - \frac{k + K}{K}\right) \langle x \rangle_X^2 \\ &= \frac{1}{2} \frac{k^2}{K} \langle x \rangle_X^2. \end{aligned} \quad (30)$$

We obtain therefore the difference ΔF of the *internal* free energy $F = E - TS = (\langle H \rangle - U) - TS$:

$$\Delta F = \Delta G - \Delta \langle U \rangle = \frac{1}{2}k \langle x \rangle_X^2. \quad (31)$$

We see that, with the correct application of the thermodynamic relations, it is possible to reconstruct the internal (free) energy landscape.

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